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ABSTRACT

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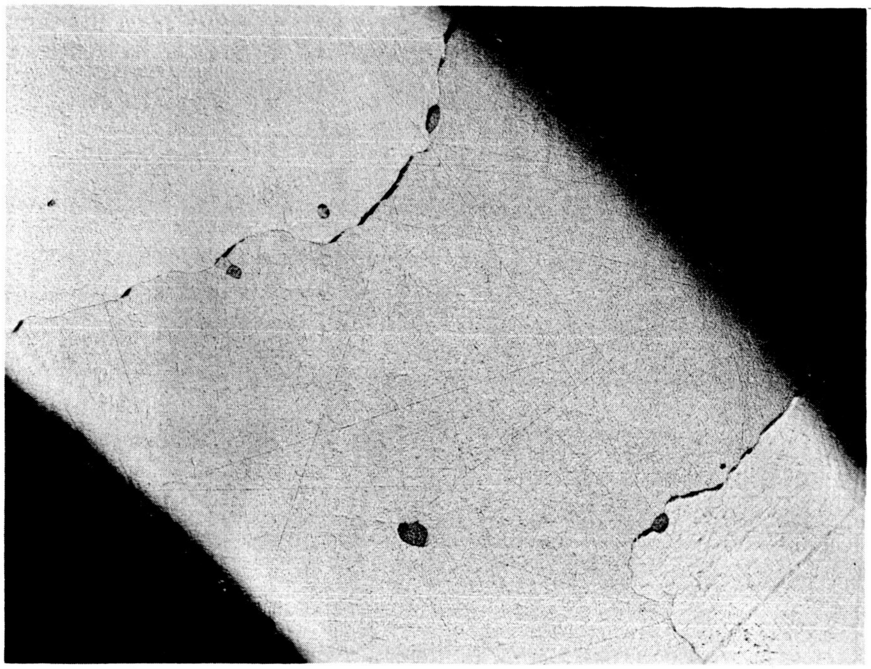
Tungsten prepared by vapor-deposition techniques is generally quite resistant to grain growth. Experimentation has shown that this resistance to grain growth is primarily related to a lack of driving force rather than to pinning of the grain boundaries by impurities; i.e., the material is deposited with a very highly oriented structure having low angle boundaries between the grains and is in a relatively stress free condition. In all cases where grain growth is observed, it is initiated at a layer of small, equiaxed, randomly oriented grains which extends into the deposited material up to 0.003 in. from the substrate surface. When growth has started in this layer, it then progresses, much like a wave front, through the remainder of the specimen. If this layer is removed prior to thermal treatment, resistance to grain growth is markedly improved.

Author

INTRODUCTION

Early in the development of high-temperature nuclear fuels (i.e., for operation at 1800°C or above), it became evident from considerations of the compatibility of prospective fuel materials with various candidate metallic cladding materials[1,2,3] that no matter which fuel was considered (carbides or oxides), only tungsten (or perhaps in the case of oxides, tungsten based alloys) qualifies as a satisfactory material for long time operation. However, when the fabrication of experimental assemblies was attempted with the use of conventional tungsten, it was not possible to maintain the structural integrity of thin sections when the parts were cooled after initial operation, because extensive grain growth caused severe embrittlement and a loss of resistance to thermal or mechanical shock. On the other hand, tungsten prepared by the hydrogen reduction of WF_6 was generally found to be quite resistant to grain growth, and its mechanical characteristics appear to be quite stable even after thermal treatments up to 1200 h at 1800°C and after shorter times at temperatures up to 2500°C.

Figure 1 shows a comparison of the grain growth characteristics of a conventional powder-metallurgy-based extruded product and vapor-deposited tubing after an 1800°C thermal treatment. Figure 2 shows specimens from the same vapor-deposited tungsten tube after thermal treatments at higher temperatures. Although vapor-deposited tungsten made in our laboratory or obtained from San Fernando Laboratories generally exhibits the high degree of resistance to grain growth indicated above, it was observed that occasionally specimens would be encountered which exhibited extensive grain growth and that materials prepared by different laboratories showed a wide variance in their behavior at elevated temperatures.[4]



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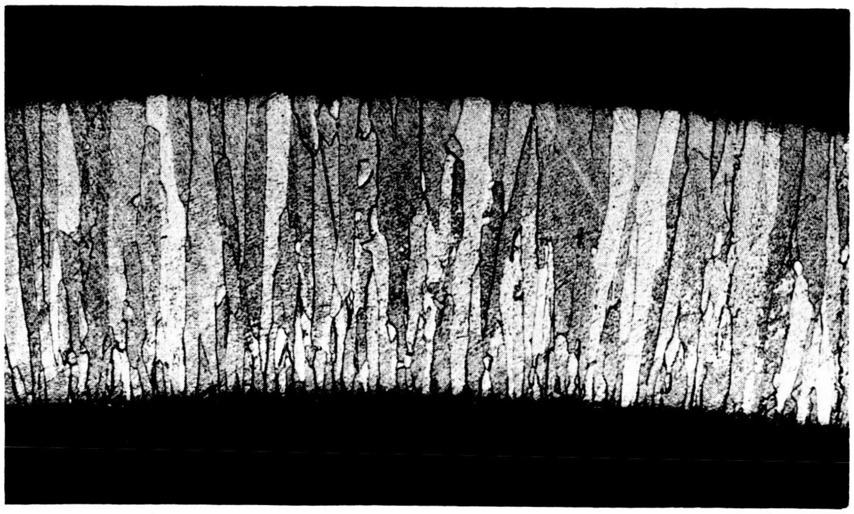
(a)



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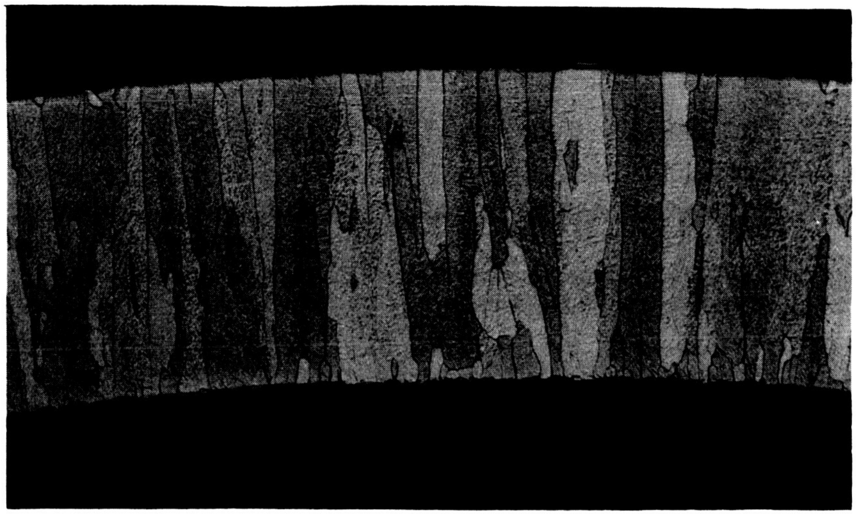
(b)

Fig. 1--Comparison of grain growth in extruded and vapor-deposited tungsten tubing after 100 h at 1800°C; (a) extruded tubing; (b) vapor-deposited tubing



M8537-1 100×

(a)

M8584-1 100×

(b)

Fig. 2--Resistance of vapor-deposited tungsten to grain growth; (a) after 15 h at 2200°C; (b) after 1 h at 2500°C

The lack of predictability as to whether or not a given specimen of vapor-deposited tungsten would exhibit grain growth led to confusion and uncertainty in the use of this material. This paper presents the results of some experiments which were designed to gain a greater understanding of the behavior of this material, and thereby lead to greater confidence in its use.

EXPERIMENTAL PROCEDURES AND RESULTS

The resistance to grain growth of vapor-deposited tungsten could be attributed to either or both of two possible mechanisms:

1. Grain boundary pinning--although the tungsten is quite pure (see Table I), it would be possible for those impurities which are present to be segregated at the grain boundaries and thus prevent grain boundary migrations.
2. Lack of driving force--tungsten formed by chemical vapor-deposition is relatively strain-free and quite highly oriented, with the most common orientation being the {100} planes parallel to the substrate surface.[5, 6] This means that only low angle grain boundaries exist, and therefore in the absence of the introduction of mechanical strain, there would be no driving force to initiate grain growth.

Because observations had indicated that once grain growth was initiated it appeared to proceed without much impedance, it was thought that the first mechanism, grain boundary pinning, was not the controlling factor. This was proven when two tubes were obtained from San Fernando Laboratories which had essentially the same concentrations of impurities (see Table II), but whose resistance to grain growth was markedly different. These tubes differed in the mode of deposition, one being deposited on a male mandrel (i. e., on the outside diameter of a cylindrical form) and the other in a female mandrel (i. e., on the inside diameter of a tubular

Table I

TYPICAL PURITY OF VAPOR-DEPOSITED TUNGSTEN

Element	Concentration (ppm)	Element	Concentration (ppm)
O_2	< 10	Mg	0.5
N_2	< 15	Mn	N < 0.5
C	6-10	Mo	N < 100
H_2	2-4	Na	N < 20
F	5-10	Ni	N < 1
Ag	N < 0.5[a]	Pb	N < 4
Al	N < 1	Rb	N < 2
As	N < 20	Sb	N < 6
B	N < 4	Si	< 2
Ba	N < 2	Sr	N < 20
Ca	N < 10	Te	N < 200
Cd	N < 8	Th	N < 80
Co	N < 1	Ti	N < 6
Cu	N < 0.5	Tl	N < 8
Fe	< 1	V	N < 8
Hg	N < 8	Zn	N < 20
In	N < 20	Zr	N < 20

[a] N = Not detected. In these cases the lower limit of detection by conventional spectrographic techniques is indicated.

Table II

COMPARATIVE CHEMISTRY OF SPECIMENS, ILLUSTRATING LACK OF CORRELATION BETWEEN CHEMISTRY AND GRAIN GROWTH

Element	Concentration (ppm)[a]	Concentration (ppm)[b]
C	6.2	6.4
O	6.5	11.5
N	5	4
H	3	4
F	9	4
Fe	< 1	< 1
Mg	0.5	0.5
Ni	N < 1	< 1
Si	< 2	2

NOTE: No other metallic impurities were detected in either specimen by spectrographic analysis.

[a] Specimen shown in Figs. 1 and 2.

[b] Specimen shown in Fig. 3.

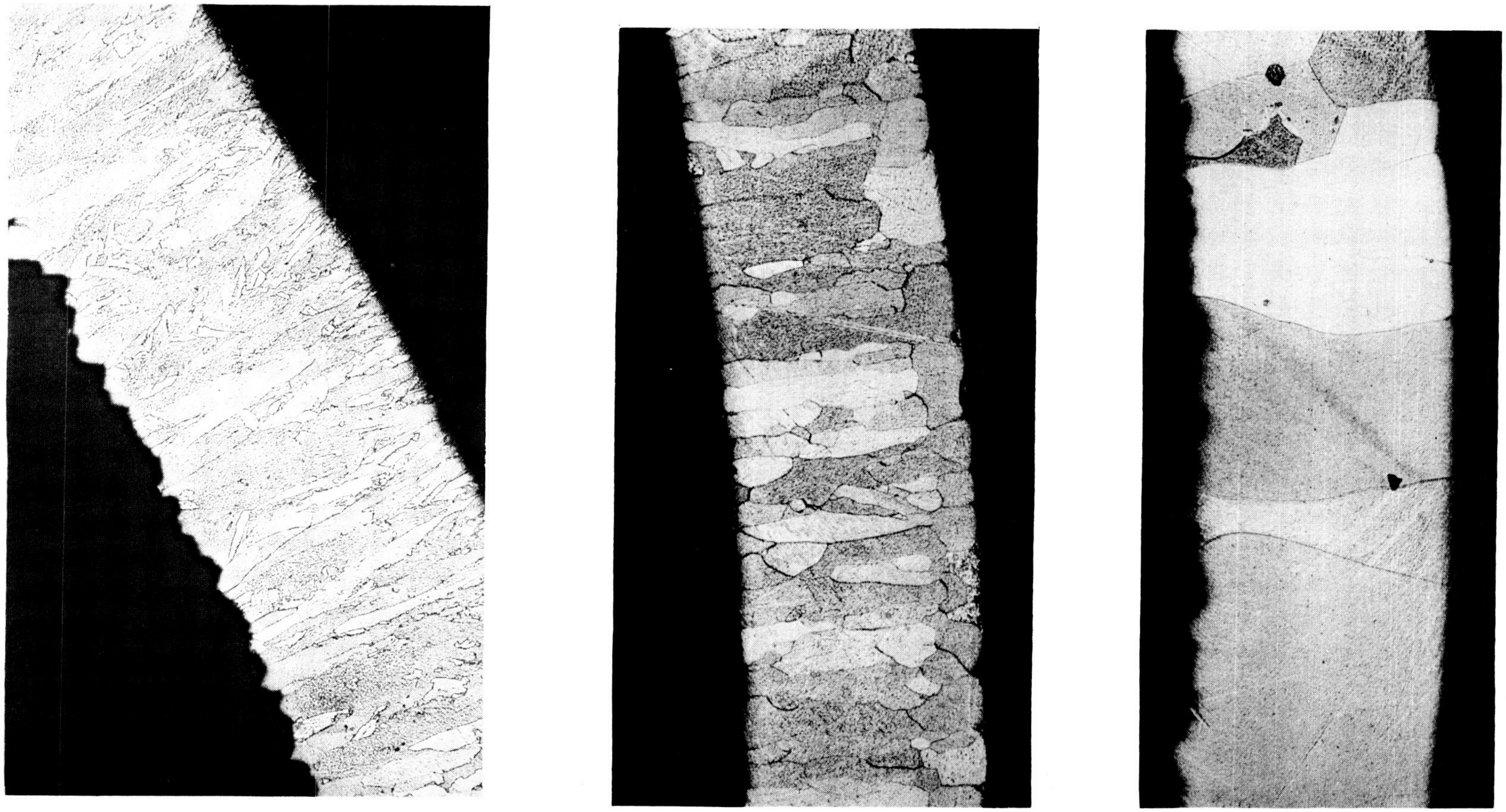
form). Figures 1b, 2a, and 2b show the structure and resistance to grain growth of the tube deposited on the male mandrel; and Figs. 3a, 3b, and 3c show the structure and grain growth behavior of the tube formed in the female mandrel. It may be noted that even though the only significant difference in composition is a somewhat higher oxygen concentration in the tube formed in the female mandrel, this tube had little resistance to grain growth as compared to the tube formed on the male mandrel. This indicates that, at least in this case, tubes having the same composition could differ greatly in resistance to grain growth, and therefore some mechanism other than grain boundary pinning must be controlling this phenomenon.

To assess the importance of the second proposed mechanism, and especially the role of a highly preferred orientation in minimizing the driving force for grain growth, samples were prepared with controlled variations in the tilt angle between grains. Two types of specimens were prepared utilizing the tendency for the grains formed during vapor deposition to grow perpendicular to the substrate surface.

The first type of specimen was formed on a nickel male mandrel having a variety of longitudinal discontinuities machined in its surface. These were designed to produce both concave and convex discontinuities in the deposit and both sharp notches and gradual changes in the section.

By providing a variety of discontinuities, and thereby, because of growth morphology, a variety of grain boundary angles about the periphery of one specimen, the possibility of effects due to differences in composition is eliminated.

The second type of specimen was based on the observation that small diameter tubes exhibited more grain growth than large diameter tubes. It was thought that this could be associated with the fact that small diameter tubes have larger tilt angles between the grains than large diameter tubes, because of the dual requirement for the grains to grow perpendicular to the substrate surface and yet maintain a continuous coating about the entire



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M8250-1 100× (b)

M8585-1 100× (c)

Fig. 3--Grain growth characteristics of vapor-deposited tungsten formed in a female mandrel; (a) as received; the outer diameter is the region which was in contact with the mandrel during deposition; (b) after 100 h at 1800 $^{\circ}$C; note that the equiaxed grains are beginning to grow at the outer diameter; and (c) after 1 h at 2500 $^{\circ}$C

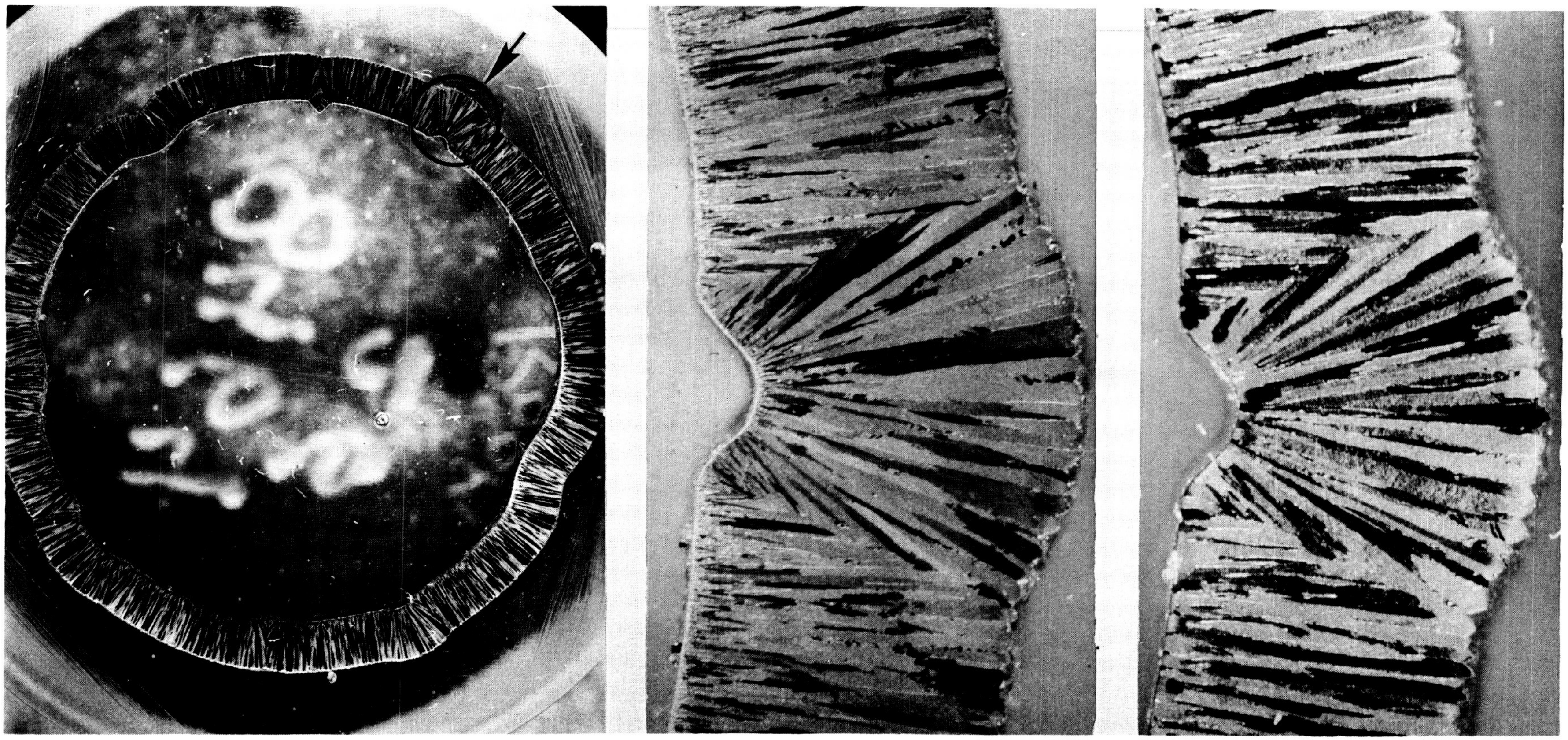
periphery of the mandrel. To study this in a controlled fashion, tubes of four sizes were prepared: 1/16, 1/8, 1/4, and 1/2 in. in diameter.

Transverse sections were cut from the tubes containing the longitudinal discontinuities and from each of the tubes representative of the four diameters. These specimens were then subjected to thermal treatments and their resistance to grain growth was observed.

Figure 4a shows a section cut from a tube containing longitudinal discontinuities in the as-deposited condition. The wide variety of grain boundary angles which was obtained can be observed, and it may be noted that in many areas the tilt angles exceeded the 10 to 30 degrees associated with the saturation of surface energy as a function of grain boundary angle.[7] In Fig. 4b a representative area is shown at a higher magnification to show the detail of the resultant grain structure. Figure 4c shows a similar area from a section which was thermally treated for 1 h at 2500°C. Quite unexpectedly, as shown in Fig. 4c, no grain growth resulted even about the most severe discontinuities.

The tests performed on the tubes of varied diameters also showed unexpected results. It was found, as expected, that the 1/16 and 1/8 in. diameter tubes showed little resistance to grain growth, while the larger diameter tubes showed a more stable grain structure. However, the mode of grain growth was unusual and is illustrated in Fig. 5 for the 1/8 in. diameter tube. Figure 5a shows that after 15 h at 2000°C, small equiaxed grains are observable at the specimen inner diameter; and Fig. 5b shows that after 1 h at 2500°C, these small grains appear to be growing into the specimen in a wave-like manner and consuming the columnar grains. It is important to note that the tilt angle between the columnar grains appear to have little effect, if any, on the process. Referring again to Fig. 3b, it can be observed that in this case grain growth also appears to have started on the surface where the initial deposition occurred and then to have proceeded in a wave-like fashion through the remainder of the specimen.

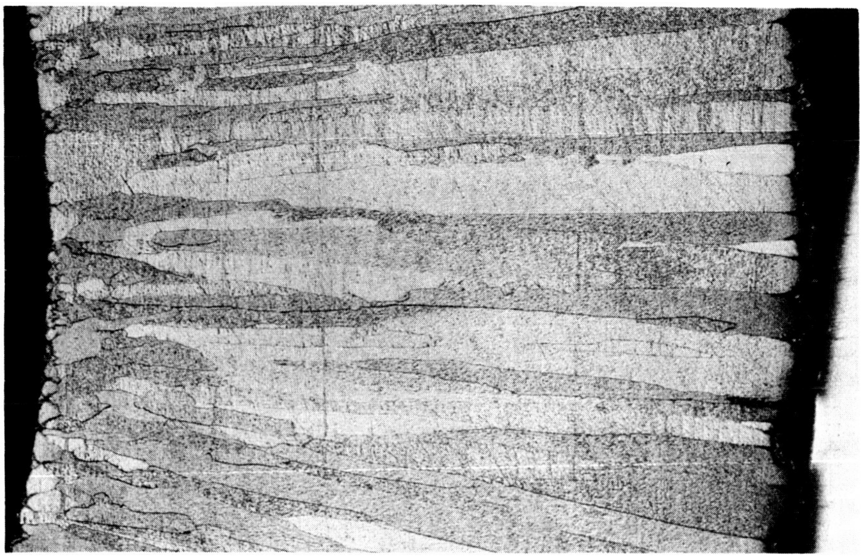
Other occurrences of grain growth in vapor-deposited tungsten were reviewed and in all cases where the growth had stopped before the columnar



M-8464-2-1 (20×) M-8603-4 (20×)

(a) (b) (c)

Fig. 4--Grain growth characteristics in a specimen deposited on a mandrel having longitudinal discontinuities which cause regions of large angle tilt boundaries; (a) over-all tube; as deposited; (b) representative area; and (c) representative area after 1 h at 2500°C; note the absence of grain growth even in regions of high angle tilt boundaries



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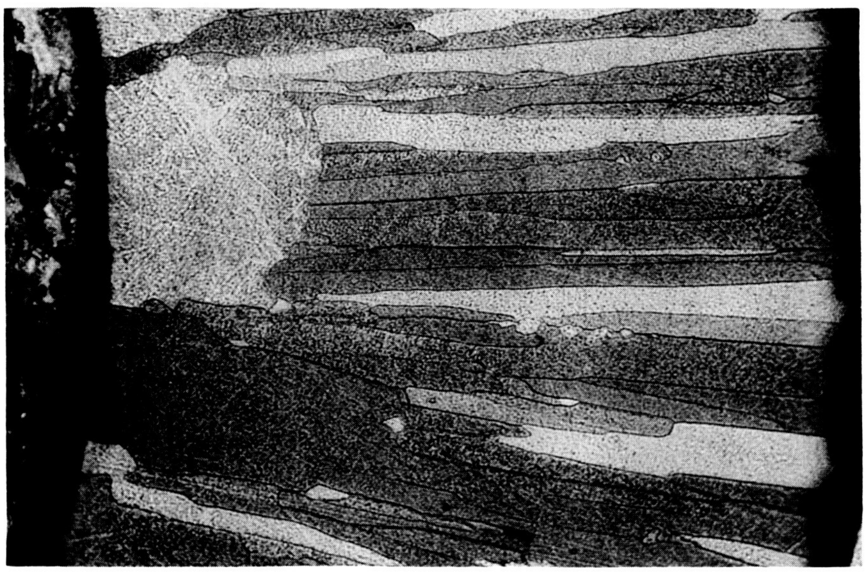
(a)



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(b)

Fig. 5--Grain growth in a 1/8 in. diameter tube; (a) after 15 h at 2000°C; note the small, equiaxed grains on the inner diameter; (b) after 1 h at 2500°C; note that the small, equiaxed grains have grown and are moving through the remainder of the specimen much like a wave front

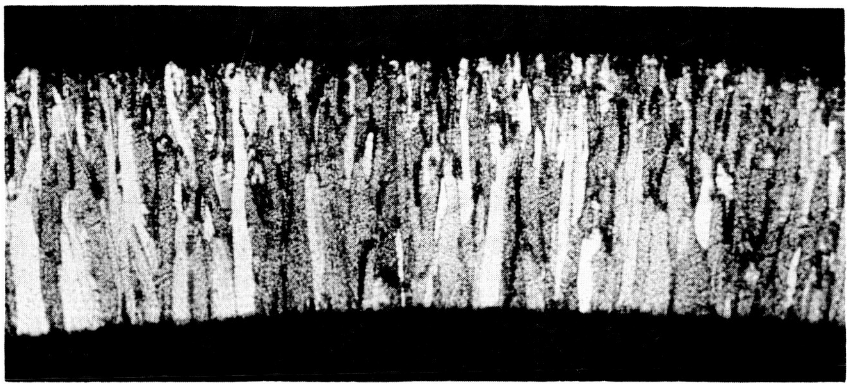
structure disappeared completely, the same pattern was followed: growth beginning at the surface where deposition started and then proceeding throughout the rest of the specimen. It was postulated that the initial growth was associated with a thin (normally less than 0.003 in.) layer of randomly oriented, equiaxed grains found in the region of initial deposition. Figures 3a, 6a, and 6b illustrate this layer for three tubes representative of deposition on both male and female mandrels.

Since grain growth was always initiated at this layer of randomly oriented grains, it was further postulated that if these grains were removed, then resistance to grain growth should be markedly improved. To test this postulate, sections of the tubes shown in Figs. 6a and 6b were electropolished to remove about 0.005 in. from the surface on which deposition had begun, thereby removing the randomly oriented grains. Figures 7 and 8 indeed show that removal of these grains has improved the materials' resistance to grain growth and the postulate is thereby verified.

DISCUSSION

It has been shown that the lack of a driving force, rather than pinning of the grain boundaries by impurities, is the controlling factor in determining the resistance of vapor-deposited tungsten to grain growth at elevated temperatures. It was further determined that when grain growth has been observed, it has started at regions of significant grain misorientation--primarily a layer of small, equiaxed, randomly oriented grains formed during the initial stages of deposition on the substrate surface. Once growth has started, it then appears to move like a wave front through the remainder of the specimen, consuming the columnar grains in its path. It was observed that if this layer of fine, randomly oriented grains was removed prior to thermal treatment, then the resistance of the material to grain growth was markedly improved.

These observations were made on tubing which was not mechanically strained, and the influence of such strains either prior to thermal treatment



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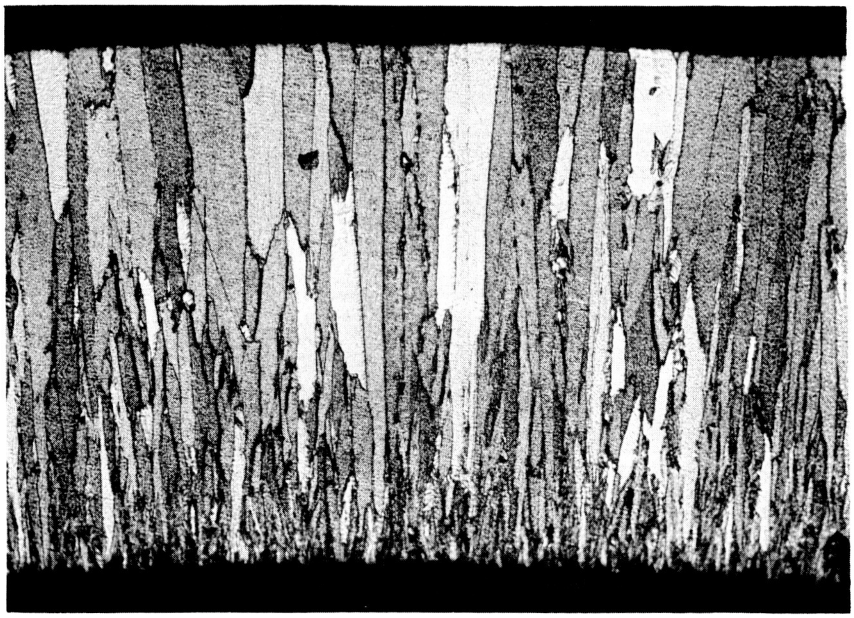
(a)



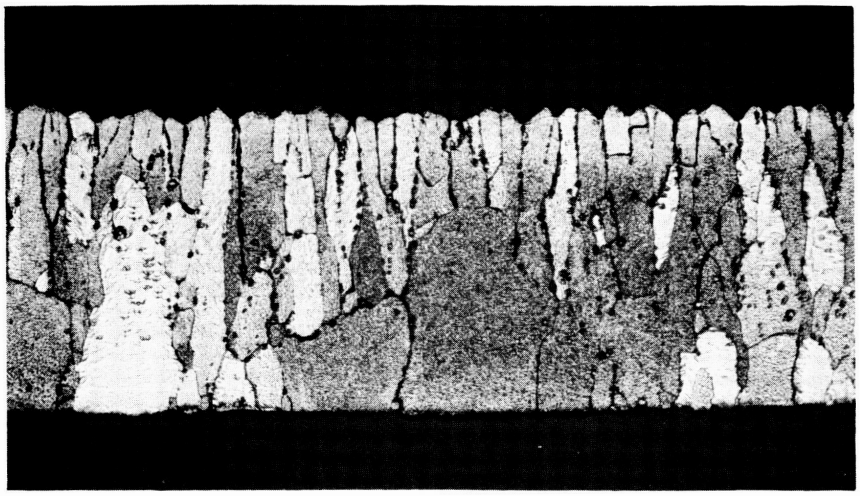
M9905-1 135×

(b)

Fig. 6--As deposited tungsten tubing illustrating the formation of fine, randomly oriented, equiaxed grains during the early stages of deposition; (a) tubing prepared in a female mandrel; outer diameter is region of initial deposition; (b) tubing prepared on a male mandrel; inner diameter is region of initial deposition

M10036-1 135×

(a)



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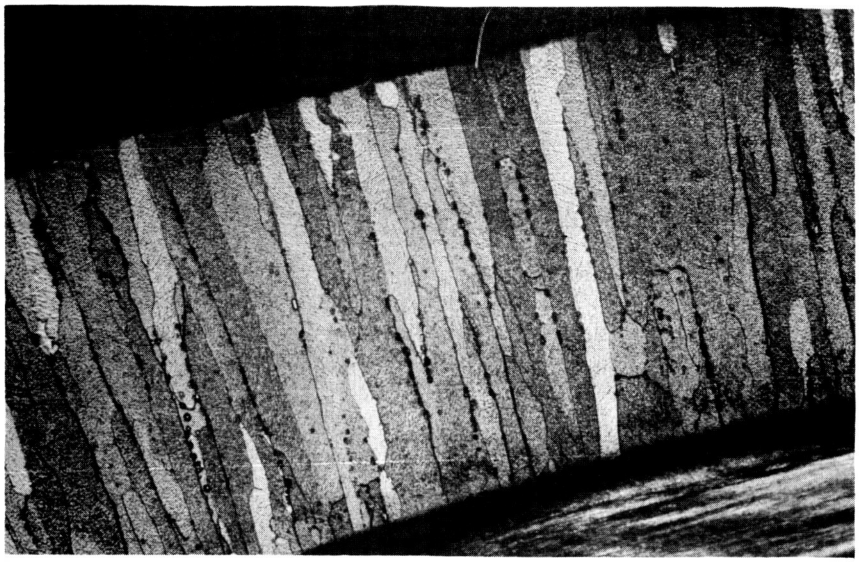
(b)

Fig. 7--Influence of electrolytically removing the layer of fine, randomly oriented grains on the resistance to grain growth of tubing formed in a female mandrel after 11 h at 2500°C; (a) electropolished; (b) not electropolished; note that grain growth started on outer diameter, the region in contact with the mandrel during deposition



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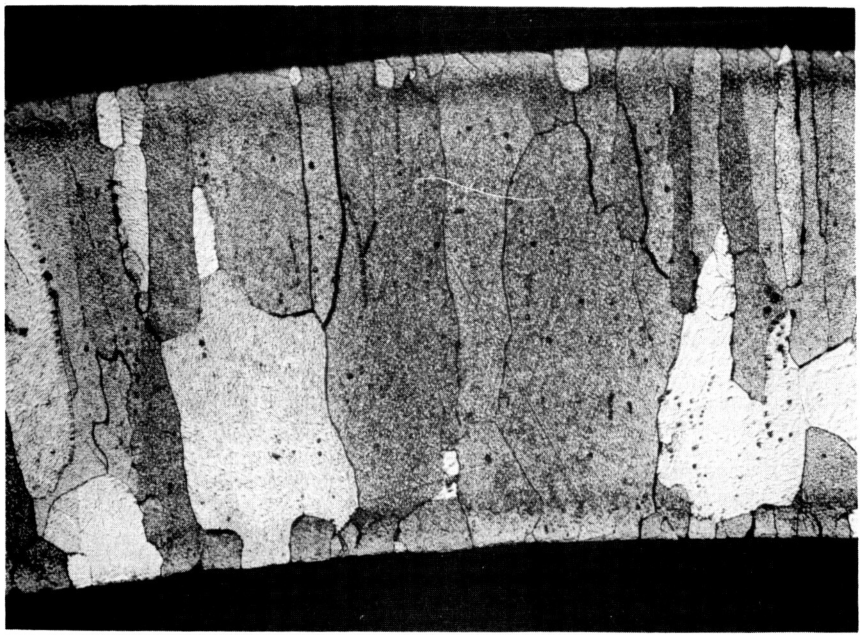
(a)



M10035-1 135×

(b)

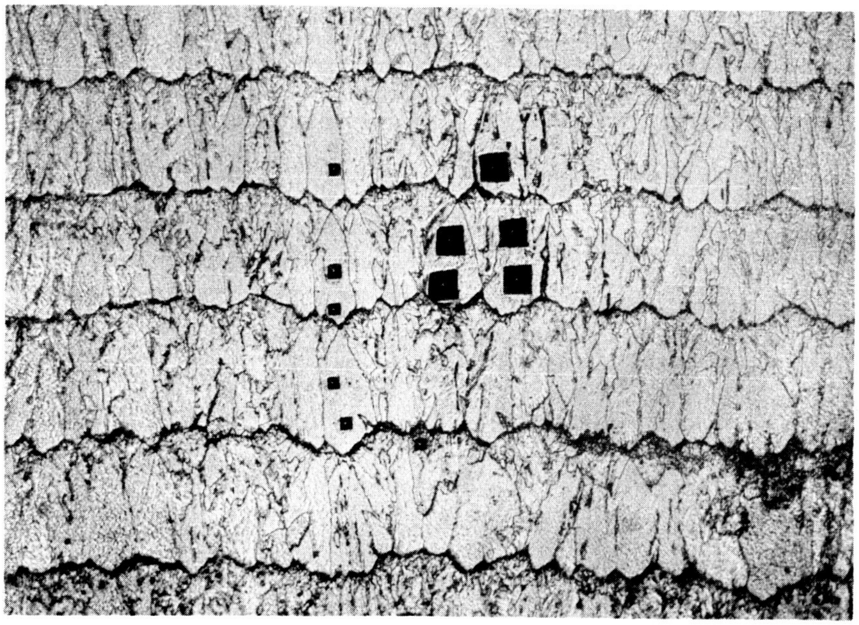
Fig. 8--Influence of electrolytically removing the layer of fine, randomly oriented grains on the resistance to grain growth of tubing formed on a male mandrel after 11 h at 2500°C; (a) electropolished; (b) not electropolished; note that grain growth started at inner diameter

or at temperature (creep) is unknown. It must also be emphasized that these observations, in particular those with regard to the lack of a grain boundary pinning effect, were made on relatively high purity tungsten and could be changed by the intentional (or unintentional) introduction of higher concentrations of either interstitial or substitutional elements. However, the applicability of these observations to material obtained from a wide variety of sources and representative of deposition from both WCl_6 and WF_6 (and even electrodeposition) is illustrated in Ref. 2.

Some areas which are not yet understood are:

1. Is initiation of growth in the small, randomly oriented grains associated with orientation differences, or could other effects such as residual strain or impurity concentration in this region be the controlling factor?
2. What is the cause of the randomly oriented, fine grained layer, and how can it be minimized?
3. Since some vapor-deposited tungsten is resistant to grain growth, even though it is not electropolished and does contain a thin layer of small, randomly oriented grains, what determines the magnitude of the effect exerted by these layers? Qualitatively, it appears to be associated with the thickness of this layer, but what is the critical thickness below which the effect is lost?
4. As it was demonstrated in the experiments described above that large angle tilt boundaries were not effective in initiating growth, what orientation (or misorientation) characteristics are required?
5. It has been observed that tubing of small diameter exhibits a greater susceptibility to grain growth than does tubing of large diameter; and it has also been observed[2] that tubing formed in a female mandrel has less resistance to grain growth than that formed on a male mandrel. How do these geometric considerations govern the formation or effect of the fine-grained randomly oriented layer?

While many questions remain unanswered, the information gained through these experiments is helpful in understanding the differences which have been observed between vapor-deposited tungsten specimens from different laboratories, and also helpful in the design and fabrication of more dependable items made of this material. One of the interesting areas which is influenced by these ideas is the manufacture of "fine-grained" vapor-deposited tungsten. Based on conventional metallurgical thought, there has been a great distrust of the columnar vapor-deposited structures, and efforts have been made to produce more equiaxed structures by (1) periodically interrupting the deposition process (see Fig. 9a) or (2) introducing an active metal contaminant into the gas stream during deposition[8] (the latter probably being effective by forming particulate matter with impurities in the environment and causing heterogeneous nucleation). While these types of structures may give better low temperature characteristics than the columnar structure (however, this has never been reported), one must consider what characteristics these structures will exhibit at an elevated temperature, which is the environment where tungsten's advantages are obtained. It might be expected that these "fine-grained" structures would no longer have the low level of surface energy associated with highly oriented grains which is required to prevent grain growth. In fact, it can be observed in Fig. 9a that each time a new layer is started, a new region of the fine, equiaxed grains is formed; and Fig. 9b further indicates that on thermal treatment, this layer has initiated grain growth in each stratum (which in several cases has migrated across an interruption). A further disadvantage of this process for forming fine grains can also be noted in Fig. 9b, and is related to the necessity for contamination of the surface during each interruption in order to form a stable interface. It is observed that this contamination has caused a large degree of porosity at the interruptions even after only 1 h at 2500°C, and similar porosity was found even after 2200°C thermal treatments. While porosity is also observed in Figs. 7 and 8, it was noted only after times



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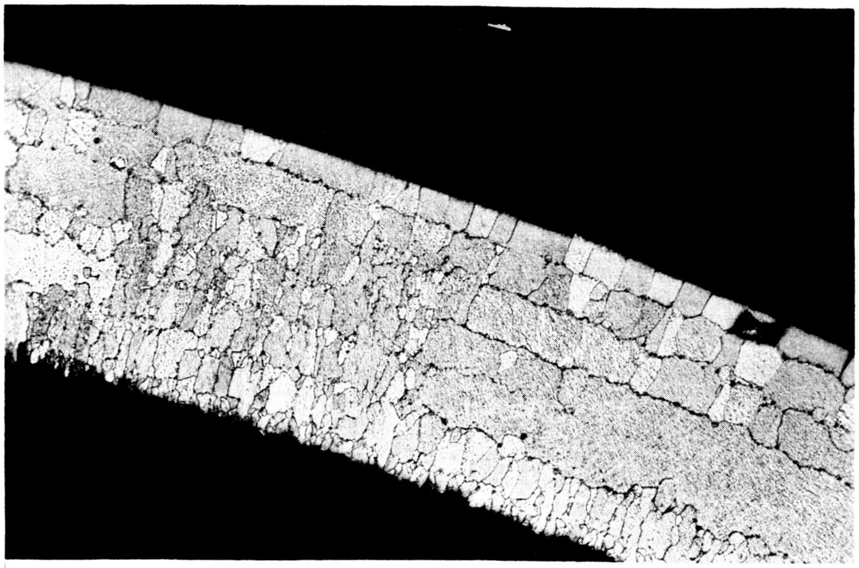
(a)



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(b)

Fig. 9--Grain growth characteristics in a specimen whose columnar structure was broken up by repeated interruptions during deposition; (a) as received; note the region of fine, equiaxed grains formed each time deposition was re-initiated; black markings are hardness impressions; (b) after 1 h at 2500°C; note grain growth within each layer, the migration across some interruptions, and the large degree of porosity at the interface between each layer

greater than 2 h at 2500°C, and not at any lower temperature. It is evident that the optimum structure of the tungsten must be related to its end use and a fine-grained equiaxed structure may not always be the best.

CONCLUSIONS

1. Vapor-deposited tungsten can exhibit remarkable resistance to grain growth for up to 11 h at 2500°C and for longer periods at lower temperatures.

2. While one cannot say that the contaminant level of the tungsten never plays a role in its resistance to grain growth, it has been demonstrated that tungsten of similar chemistry but of different structure can exhibit widely different responses to thermal treatment.

3. Structure appears to play a very important role with respect to the resistance of tungsten to grain growth, and it can be stated categorically that whenever grain growth has been observed in tungsten which has not been subjected to mechanical strain, it has started at a region of significant grain misorientation--primarily a layer of small, equiaxed, randomly oriented grains formed during the initial stages of deposition. Growth initiated in this region then proceeds in a wave-like fashion through the remainder of the material, consuming the columnar grains in its path.

4. If the layer of fine, randomly oriented, equiaxed grains is removed, grain growth is not observed to occur even after 11 h at 2500°C.

5. Tubes of small diameter (less than 1/8 in.) exhibit a greater tendency toward grain growth than do tubes of larger diameter; and tubes formed in a female mandrel are more subject to grain growth than those formed on a male mandrel.

6. The artificial formation of a fine-grained structure by the periodic interruption of the deposition process or by the addition of particulate matter to the gas stream to cause heterogeneous nucleation may impair the resistance of the material to grain growth by introducing a larger degree of grain misorientation and thereby a larger driving force for grain growth.

ACKNOWLEDGMENTS

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